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3,691,027

METHOD OF PRODUCING CORROSION RESISTANT CHROMIUM PLATED ARTICLES

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ABSTRACT OF THE DISCLOSURE

Corrosion resistant chromium plated articles and a method for producing them is provided wherein a decorative and protective multi-layer electroplate is applied on a basis metal comprising successive layers of a zinc-nickel alloy, a nickel plate and a decorative and protective chromium plate.

This invention relates to a chromium plated basis metal having a decorative and protective electroplate and a method comprising depositing on a corrodable basis metal a zinc-nickel alloy plate, a nickel plate and a chromium plate useful in the decorative and protective finishing of metals. The method of our invention permits a considerable saving in cost because of reducing the nickel content in the electroplate without sacrificing quality, beauty and corrosion resistance.

In the past it has been the practice to employ chromium as a final electroplate on basis metals especially because it retains a high luster, does not tarnish and is corrosion resistant. In the decorative-protective finishing of basis metals such as steel, copper, zinc, nickel, lead and the like, or alloys containing one or more of these as major components, it is well-known to apply multi-layer electroplates, for example, copper and/or nickel and chromium on steel; nickel and chromium on brass and copper; and copper, nickel and chromium on zinc die castings. Copper or nickel electroplates may be deposited with a dull mat surface and buffed to a mirror-like luster before receiving a bright chromium electroplate. Another common practice is to bright finish the basis metal and then apply bright electroplates. Practical methods of electrodepositing bright copper and bright nickel with a mirror-like luster which needs no buffing or coloring before receiving a chromium plate, are well-known in the art and used commercially. The brilliant mirror-like quality of the final chromium plate has become designated by the plating trade, a "bright chromium finish." Today, the bright chrome finish is expected to remain attractive for as long as the life expectancy of the article plated, whereas only a few years ago the bright chrome finish used on zinc die castings and on steel parts in outdoor service such as automobile trim, often exhibited deterioration in as short a period as 3 months under severe exposure.

Advances during the last few years have led to the development of chromium plate which will retain its "bright chrome" appearance for several years under similar severe conditions without objectionable deterioration of the basis metal. One of these methods comprises depositing the bright chromium electroplate on a so-called "duplex nickel plate" where a high degree of corrosion resistance and a bright protective chrome finish is desired. This duplex nickel plate consists of a nickel under-layer deposited as semi-bright high purity nickel, and an outer-layer of bright nickel. About 75% of the nickel is deposited in the semi-bright under-layer, and the remaining 25% in the bright nickel outer-layer, the semi-bright nickel being generally of higher purity and offering more resistance to corrosion than the bright nickel. This duplex nickel plate forms a good base for the chromium, the

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principal function of which is to provide a mirror-bright non-staining, abrasion-resistant protective finishing surface, as required in automotive trim and the like. Prior to the use of the duplex nickel plate, chromium plated articles generally consisted of a thin layer (0.25–0.75 microns) of decorative chromium over a relatively thick layer of nickel (18–30 microns) on a basis metal and sometimes over a layer of bright copper.

More recently, the corrosion resistance of chromium plated articles has been further improved by use of a so-called "micro-cracked" chromium plate. Such chromium deposits are characterized by having at least about 600 crack lines per linear inch, whereby the galvanic current developed on exposure, because of bimetallic contact, is distributed over a large area. This distribution greatly reduces the rate of corrosive penetration through the nickel to the underlying basis metal. The chromium plating baths from which microcracked chromium may be deposited are well-known in the art. See for instance U.S.P. Nos. 3,408,272 and 3,461,048. The first mentioned patent discloses a process for depositing the micro-cracked chromium in a single layer, whereas U.S.P. No. 3,461,048 discloses a process for electrodepositing a duplex micro-cracked chromium layer.

With the growing use of salt, calcium chloride and other corrosive materials for controlling snow and ice on the highways in recent years, the corrosive conditions to which the modern automobile is exposed have greatly increased. The need for relatively inexpensive high quality corrosion resistant parts, therefore, has become imperative. It has become increasingly expensive to produce such high quality parts, particularly because of the growing demand for nickel. There is, consequently, a need to substitute a part or all of the nickel under-layer with another metal (particularly if a duplex nickel under-layer has been customarily employed), while at the same time retaining all the desirable attributes of the present nickel-chromium plated article.

It is the object of our invention to provide corrosion resistant plated articles comprising a decorative and protective multi-layer electroplate on a basis metal, which is equal to present chromium plated articles at a considerable saving in cost. It is a still further object of this invention to provide a method for producing such chromium plated articles.

These and other objects of the present invention are accomplished by electroplating a basis metal with successive deposits of a zinc-nickel alloy plate containing 10–25% nickel, preferably a bright plate containing 12 to 18% nickel, followed by a bright nickel plate, and finally a bright decorative chromium plate. It has been found that an acceptable multilayer electroplate of the present invention comprises a basis metal onto which is deposited about 0.6–1.20 mils, preferably 0.80 to 1.10 mils of zinc-nickel alloy, 0.05–0.25 mil, preferably 0.10 to 0.20 mil of nickel, and 0.005–0.05 mil, preferably 0.01 to 0.03 mil, chromium, electroplated successively on a corrodable base metal.

In carrying out the process of our invention, the basis metal, such as rust-free steel, preferably is first degreased such as with a suitable organic solvent, e.g. 1,1,1-trichloroethane, after which it is rinsed with a second organic solvent miscible both with the first and with water, such as acetone, and finally with water.

Any of the conventionally employed zinc-nickel plating baths may be used if formulated or modified to give a bright plate. As noted above, the plate deposited on the basis metal should contain about 75% to 90%, preferably about 82% to 88% zinc, and about 10% to 25%, preferably about 12% to 18% nickel. Whereas the corrosion resistant properties of the multi-layer electroplate of our invention would be attained by the deposition of a

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dull nickel alloy plate as the first layer, a bright plate is preferred, where the plated article is to have a bright decorative appearance.

The zinc ions in solution in the bath may vary from 5 to 75 grams per liter, preferably from 8 to 18.5 g./l., with 12 g./l. being especially preferred. Similarly, the nickel ions in solution may vary from 1 to 40 g./l., preferably from 5.4 to 12.3 g./l. with 9 g./l. being especially preferred.

The anionic composition of the plating bath is not critical, hence any water soluble salts of zinc and nickel, or other compounds soluble in the plating bath which are commonly used in plating baths and compatible therewith, can be employed. Suitable zinc compounds include the oxide, chloride, sulfate, sulfamate, fluoborate and in some cases, acetate. Suitable nickel compounds include the chloride, sulfate, sulfamate, ammonium sulfate, carbonate, nitrate, pyrophosphate, and fluoborate. Not all of these compounds or combinations of these compounds can, however, be expected to provide deposits within the preferred range. Exemplary of a suitable zinc-nickel plating bath is that disclosed in Theory and Practice of Bright Electroplating, S. G. Bagautdinova et al., Proceedings of an All-Union Conference held in Vilnius (USSR) on Dec. 18-20 (1962)—Israel Program for Scientific Translations, Jerusalem, 1965.

In the work reported, the investigators took the formulation developed by N. T. Kudryavtsev et al. J. Appl. Chem. USSR, 35, 1035 (1962) which was formulated to provide a dull zinc-nickel protective coating on steel, and by the addition of brightening agents such as dextrine, thiourea and disulfonaphtholic acid, produced a bright zinc-nickel electroplate.

These two references are specifically incorporated herein by reference.

A suitable bright zinc-nickel alloy may be electroplated from a bath having the following composition:

Component	Concentration (grams/liter)	
	Range	Preferred
NH ₄ Cl.....	200-275	250
ZnO.....	10-23	15
NiCl ₂ ·6H ₂ O.....	22-50	36
H ₃ BO ₃	15-25	20
Dextrine (or equivalent brightener).....	(1)	5
Surfactant (M&T Anti-Pit Agent #7).....	(2)	2

¹ As required.

² As required (to reduce surface tension below 50 dynes/cm.).

The pH of the zinc-nickel alloy bath may vary from about 4-6.8, preferably 5.8 to 6.8 with a pH of 6.5 being especially preferred. The bath is operated at a temperature from about 35° to 60° C., preferably at 40° to 55° C. more preferably at 50° C., while employing current densities ranging from about 10 to 50 amperes per square foot (a.s.f.), preferably not over 40 a.s.f. Soluble anodes of zinc and nickel are employed, and in all instances the bath is continuously agitated and filtered. The plating current should be proportioned between the zinc and nickel anodes so as to maintain a constant zinc-nickel ratio in the bath between 0.5 and 1.5.

The ammonium chloride is added to the zinc-nickel alloy plating bath to increase the conductivity of the electrolyte and at a pH of about 6.5, to solubilize the zinc and nickel salts through formation of Zn(NH₃)₄⁺⁺ and Ni(NH₃)₆⁺⁺ and other soluble complexes. The ammonia released in the cathode film during discharge of the metal complexes also serves to buffer the cathode film to prevent basic metal salts from precipitating. For instance, in the absence of NH₄Cl and at a pH of 5.6, basic zinc and nickel salts are found to precipitate during alloy deposition.

Boric acid is added to the zinc-nickel alloy bath to help prevent pitting and to aid in buffering the cathode film.

Bright nickel electroplating baths are generally prepared by adding selected compounds (generally organic) to plat-

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ing baths having the same basic constituents found in standard baths, which if not so modified, would produce dull electroplates. These organic additives or "brighteners" generally function best at high current densities, and this in turn necessitates a somewhat higher nickel content. Dextrine and thiourea are found especially effective as brighteners. Among other suitable brighteners are gelatin, coumarin, naphthol disulfonic acid, saccharin, peptone, or proprietary zinc and nickel brighteners such as "Rodine 50" (Amchem Products Inc., Ambler, Pa.), and Electro-Brite No. 22 (Electrochemicals Inc., Cleveland, Ohio.) The literature relating to brighteners is very considerable, much of it dividing them into classes and sub-classes. Among them are included metal ions characterized by high hydrogen overvoltage in acid solutions, compounds of sulfur, selenium and tellurium, as well as the several classes of organic brighteners.

In addition, organic surfactants may be added to reduce the surface tension of the electrolyte. This facilitates the release of hydrogen bubbles at the cathode, and thereby minimizes pitting of the electroplate. These surfactants, or "wetting agents" also tend to increase the uniformity of the deposit, increase the covering power, and reduce the brittleness of the resulting plate by decreasing internal stress.

Many types of wetting agents are suitable, but most proprietary formulations are basically anionic in character. Among the satisfactory wetting agents are sodium lauryl sulfate, alkyl substituted benzene sulfonates, sodium lauryl sulfoacetate, sodium monolaurin monosulfate, the sodium salt of lauric acid monoester of diethylene glycol, dodecylmethane sulfonate and the proprietary "M & T Anti-Pit Agent No. 7" which we prefer, and which is marketed by M & T Chemical, Inc. of Rahway, N.J.

The quantity of surfactant added to the plating bath should be sufficient to reduce and maintain the surface tension of the electrolyte below 50 dynes/cm. at 50° C., as measured by the stalagmometer or by any other equivalent method. The stalagmometer is essentially a glass capillary tube having a bore of 0.5 mm. and a bulb or reservoir near its midpoint. The lower end of the capillary is ground to a perfect flat surface. The instrument is filled with distilled water and the number of drops of water counted for the volume between two marks on the tube. A sample of the plating bath is then taken, and the number of drops for the same volume counted. The following formula is applied:

$$\text{Surface tension in dynes/cm.} = \frac{W \times \text{Sp. Gr. of unknown}}{\text{No. drops of unknown}}$$

where W=73× the number of drops of water at 25° C.

The ratio of zinc to nickel in the alloy plate is affected by changes in the ratio between the zinc and nickel ions in the bath, by the current density (CD), and by the bath temperature, but the effect is highly complex. The trend of alloy composition with temperature cannot be said to have a definite direction, but rather depends on the range of current density used. Increasing the current density may increase the zinc content of the electroplate, may cause it to decrease, or to remain constant, depending on various factors. Normally, for example, one might expect an increase in the current density to be reflected by an increase in the zinc content of the plate, since zinc is the less readily deposited metal, but at high current densities the cathode diffusion film readily becomes depleted in zinc, and the alloy deposition becomes controlled by diffusion, which is further modified by the degree of agitation in the bath. This is particularly true with baths low in zinc.

Within the conditions and ranges which we employ, an increase in the zinc content of the bath results in a corresponding, although not marked, increase in the zinc content of the alloy electroplate. Increasing the temperature to 60° C. when the current density is relatively low (17 a.s.f.), results in a marked increase in the nickel

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content of the plate. When the temperature is maintained at this figure, and the current density is increased to 50 a.s.f., however, the percent nickel in the plate drops to 18.8%. Variations in the concentration of the metallic ions present in the bath, or variations in the current density at temperatures between 40 and 50° C., have comparatively little effect on the percentage composition of the alloy plate. The table of Example 2 illustrates these relationships.

In order to improve adhesion between the zinc-nickel plate and the overlaying nickel plate, it is desirable to treat the zinc-nickel deposit with an "activating" bath to prepare the surface for the subsequent nickel deposit. For instance, a bath containing 0.2-0.4 grams of ammonium bifluoride per liter of 1.5 to 2.0% sulfuric acid has been successful when used at a temperature of about 20° to 30° C. The basis metal after having received the zinc-nickel plate is rinsed with water and then preferably, immersed in the activating bath for a short period of time, e.g. in the order of about 1 minute, after which a final water rinse is applied.

The nickel plate which is used to coat the zinc-nickel alloy may be deposited from any one of several commercial bright nickel baths. The variations are many, and the literature covering the art, voluminous because of the importance of nickel electrodeposition methods. Exemplary of suitable bright nickel plating baths are those disclosed in U.S. Pats. 3,366,557; 3,352,766; 3,349,015; 3,341,433; 3,334,032 and 3,305,462. There are also available suitable proprietary bright nickel baths such as the preferred "Electro-Brite," marketed by Electro-chemicals Inc., Cleveland, Ohio. This bath is operated at a cathode current density of about 50 a.s.f. in accordance with the manufacturer's instruction to obtain a bright nickel electroplate of 0.1 to 0.2 mil. About 2 to 4 minutes are required.

Bright nickel plating baths in commercial use frequently are modifications of the original Watts nickel electroplating bath (O. P. Watts, Trans. Amer. Electrochemical Soc. 23, 99 (1913), the modifications consisting essentially of the addition of so-called organic brighteners and anti-pitting agents to the bath. Typically, these baths, which generally are operated at temperatures between 30 and 65° C., preferably 45° to 60° C., contain $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ in concentrations of 200 to 400 g./l.; $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in concentrations of 30 to 120 g./l.; H_3BO_3 in concentrations of 30 to 50 g./l.; a small quantity of an organic surfactant or "wetting agent" and relatively small quantities of one or more brightening agents. The quantities of the latter two types of additives to be used in a plating bath varies with the agent selected, of which there are many. Several are disclosed in the above patents. Additional brighteners are other additives are disclosed in the following two papers: "The Mechanism of Formation of Bright Nickel Deposits" by Yu. Yu. Matulis et al., pp. 29-34; and "Bright Nickel Plating in an Electrolyte Containing Additions of Coumarin and P-Toluenesulfonamide" by N. A. Silaeva, pp. 54-57. These papers appear in Theory and Practice of Bright Electroplating, to which reference has previously been made.

The nickel plating bath should be maintained at a pH of 1.5 to 5.8 and at a cathode current density of 18-94 a.s.f., with the bath containing 47-107 g./l. of nickel ions.

In most bright nickel plating baths, including those that are modifications of the Watts bath, the major portion of the nickel ion content is contributed by nickel sulfate hexahydrate. This nickel compound is chosen because it is the least expensive salt of nickel with a stable anion that is not reduced at the cathode, oxidized at the anode, or volatilized. It is also very soluble and readily available commercially. The anionic composition of the nickel plating bath is not critical, however; hence, any compound of nickel which is soluble in the plating bath and compatible with all its constituents can be used.

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Chloride ions may be added as sodium chloride, or perhaps more conveniently as nickel chloride. The principal function of the chloride ion is to improve anode dissolution by reducing polarization. It also serves to increase the electrical conductivity of the bath, and to increase leveling and "throwing power," (the ability of a bath to produce deposits of more or less uniform thickness on cathodes having macroscopic irregularities).

Boric acid, as in the case of the zinc-nickel alloy plating bath, serves as a buffer, particularly to control the pH in the cathode film. It also serves to maintain the pH of the bath within the operating range, the maximum buffering action being obtained at a pH of 5-6.

Surfactants or "wetting agents" are employed to prevent pitting in all types of nickel plating baths. Suitable anti-pitting agents in addition to those previously mentioned in connection with the zinc-nickel alloy bath, are disclosed in U.S. Pats. 2,254,161; 2,389,135; 2,389,179; 2,389,180; 2,389,181 and in many others. Many proprietary anti-pitting agents are marketed, such as M & T Anti-pit Agent #7, to which reference has previously been made.

In all instances, it is preferable that the plating baths be agitated and continuously filtered.

Watts-type plating baths, the components of which fall within the ranges previously indicated, may be employed without the organic brightening agents to produce a dull mat electroplate. Proprietary baths are also available such as "Permalume G." This bath, which is marketed by the Hanson-Van Winkle-Munning Co. of Matawan, N.J., is operated at a cathode current density of 50 a.s.f. It utilizes proprietary addition agents and produces a semi-bright plate. Although the use of such deposits as an underlayer for the final chromium electroplate will not lead to the preferred embodiment, which is a final coat of bright, mirror-like, decorative chromium, a satisfactory corrosion resistant system can nevertheless be obtained.

The basis metal, after having received both the zinc-nickel alloy plate followed by the activating bath and the nickel plate, is rinsed with water, and given a final chromium plate.

This chromium plate, applied as a finishing coat to the plated article, may be deposited from any one of several commercial chromium plating baths but preferably from one which will give a conventional chromium electroplate having in the order of 700 cracks per linear inch.

It is well-known that the use of so-called micro-cracked electrodeposited chromium coatings confer excellent corrosion protection to metal undercoats and/or the basis metal, by distributing the galvanic charges that develop due to dissimilarity of the contacting metals.

There are many commercial baths which will provide a suitable micro-cracked bright chromium plate. Some such baths are disclosed in U.S. Pats. 2,800,438; 3,157,585; 3,408,272 and 3,461,048.

Typically, the chromium plating bath should be maintained at a temperature of 30° to 100° C. and at a cathode current density from 70 to 1200 a.s.f., with the bath containing 57 to 583 g./l. of chromic acid. The baths preferably are operated at temperatures between 30-70° C. and at current densities between 150-200 a.s.f., contain chromic acid (CrO_3) in concentrations of 100 to 500 g./l.; sulfate ion in concentrations of 0.75 to 1.5% of the weight of the CrO_3 used, and fluosilicate ion, preferably in concentrations of from 2.0 to 7.2 g./l. A plate thickness of from 0.01 to 0.05 mil is preferred. During the plating operation, the bath should be agitated.

Since commercial chromic acid generally contains minor amounts of sulfate ion as an impurity, the quantity present should be determined and applied against the sulfate ion to be added as sulfuric acid.

It will be observed that equivalent procedures may be substituted for all steps except those of electroplating the zinc-nickel alloy, and of applying the activating rinse which precedes the deposit of the nickel plate. Plating times may also be varied, as will be apparent to skilled

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electroplaters, to produce a system meeting the broader scope of this invention as previously defined.

We believe this combination of materials to be novel.

The zinc-nickel alloy plate is characteristically about the same thickness as the semi-bright nickel customarily used, while the bright nickel is characteristically somewhat thinner. It is obvious that material savings will arise from the reduction in thickness of the bright nickel but more significantly, from the extent to which nickel is replaced by zinc in the alloy system. Inasmuch as the preferred alloy composition of this invention contains only 10-25% nickel, the savings are substantial. In a system coming within the claims of this invention, about 75-80% of the nickel normally used is essentially replaced by the less expensive and more abundant zinc. In order to produce a zinc-nickel alloy, bright nickel, chromium, multi-layer composite having both good corrosion resistance and an attractive appearance, both the composition of the zinc-nickel alloy and the quality of the alloy deposit must be carefully controlled. Variables such as bath composition, pH, temperature, cathode current density, and bath additives, all affect the composition and quality of the alloy electroplate. The nickel content of the zinc-nickel alloy should fall between 10 and 25%, for below 10% there is a significant loss, of corrosion resistance, whereas alloy plates having a nickel content in excess of 25% tend to be brittle. Another factor in the development of the zinc-nickel alloy, bright nickel, chromium composite, is the rate of deposition of the underlying zinc-nickel alloy. Since the alloy layer is essentially replacing the semi-bright nickel layer of the duplex nickel-chromium composite, their rates of deposition should be competitive.

EXAMPLE 1

Zinc-nickel alloy deposit

A series of runs are made in which zinc-nickel alloys are deposited on low-carbon steel cathodes as the basis metal, to determine the effect on the composition of the alloy plate, as the following factors are varied:

- (1) the zinc-nickel ratio in the bath,
- (2) the plating temperature, and
- (3) the cathode current density.

The apparatus employed comprises a 15 liter cylindrical plating tank within which the cathode, consisting of a 6-inch solid, low-carbon steel rod, $\frac{3}{4}$ inch in diameter, is axially and rotatably mounted, so as to obtain uniform deposits. Four rectangular anodes are distributed symmetrically around the cathode. Two of these are fabricated from $\frac{1}{4}$ inch rectangular nickel anode stock (99% Ni minimum), having a total area of 0.88 ft.², and two fabricated from $\frac{1}{4}$ inch rectangular zinc anode stock (99.99% Zn), having a total area of 0.6 ft.².

The bath temperatures are maintained at the desired level by a thermo-regulator, and the baths are provided with mechanical agitation means and filtering means.

Direct current is supplied from a low voltage rectifier, and distributed to the two pairs of anodes in the proportion necessary to maintain the desired constant zinc-nickel ratio in the bath.

All zinc-nickel deposits are obtained in baths having the following nominal composition:

Component:	Concentration
ZnO	g./l. 15
NiCl ₂ ·6H ₂ O	g./l. 36
NH ₄ Cl	g./l. 250
H ₃ BO ₃	g./l. 20
Dextrine	g./l. 5
Anti-pitting agent ¹	ml./l. 1.5
Zn:Ni ratio	1.35

¹ M & T Anti-pit Agent #7 (M & T Chemical Inc., Rahway, N.J.) was used and found satisfactory as an anti-pit agent.

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In the first five runs the zinc-nickel ratio is varied in order to demonstrate the effect on the composition of the alloy. The bath is operated at a temperature of 50° C., a cathode current density of 45 a.s.f. and a pH of 6.4. All components and all operating conditions are maintained, except for the weight of the zinc oxide, which is varied as follows, to provide the desired Zn/Ni ratios: (1) 6.4 g./l.; (2) 8.97 g./l.; (3) 11.63 g./l.; (4) 11.85 g./l.; and (5) 13.74 g./l. These quantities provide Zn/Ni ratios of: (1) 0.58; (2) 0.81; (3) 1.05; (4) 1.07 and (5) 1.24 respectively. These ratios and the operating conditions appear in the table to follow.

In order to demonstrate the effect operating temperatures have on the composition of the Zn/Ni alloy, runs 6, 7 and 8 are made, with temperature as the only variable.

In order to demonstrate the effect the cathode current density has on the composition of the Zn/Ni at each of three different temperature levels, runs 9 through 16 are made with three different cathode current densities at 40° C., two at 50° C., and three at 60° C. The percent nickel found in the alloy under these various conditions is summarized in the following table:

EFFECT OF PROCESS VARIABLES ON COMPOSITION OF Zn/Ni ALLOY

Run Number:	Zn/Ni ratio (bath)	Temp., ° C.	pH	a.s.f.	Percent Ni in alloy
1	0.58	50	6.4	45	17.0
2	0.81	50	6.4	45	16.0
3	1.05	50	6.4	45	15.0
4	1.07	50	6.4	45	16.0
5	1.24	50	6.4	45	15.5
6	1.35	40	6.3	17	16.1
7	1.35	50	6.3	17	20.0
8	1.35	60	6.3	17	48.9
9	1.35	40	6.3	17	19.1
10	1.35	40	6.3	25	16.8
11	1.35	40	6.3	50	14.4
12	1.35	50	6.3	40	16.0
13	1.35	50	6.3	50	14.0
14	1.35	60	6.3	17	48.9
15	1.35	60	6.3	30	20.3
16	1.35	60	6.3	50	18.8

The following conclusions are drawn:

A substantial change in the Zn/Ni ratio in the bath produces a relatively small change in the nickel content of the alloy deposit (runs 1-5).

A substantial increase in the nickel content of the alloy deposit is obtained as the bath temperature is increased, e.g. the deposit at 60° C. contains 48.9% nickel, but is very brittle (runs 6-8).

An increase in the cathode current density effects a decrease in the nickel content of the resulting alloy. The exact is opposite to that produced by an increase in temperature, so that at a temperature of 60° C., and a cathode current density of 50 a.s.f., the effects essentially serve to cancel each other, and the nickel content is about equal to that which might be expected at a lower temperature (40° C.), and current density (17 a.s.f.). At the 60° C. temperature and 50 a.s.f. current density, the plate is not bright, however, whereas at 40° C., and a current density of 17 a.s.f. a satisfactory bright plate is obtained.

It is concluded that the bath should be operated at a constant temperature and below 60° C. in order to obtain an alloy deposit of consistent composition even where there is a variation in the cathode current density. Good quality zinc-nickel alloy plate can be deposited at 50° C., preferably at a current density of 40 a.s.f. or below. The plating speed is essentially competitive with that of commercial semi-bright nickel deposition (50 a.s.f.).

EXAMPLE 2

In order to provide a comparison between test pieces plated by the usual commercial duplex nickel-chromium process, and test pieces plated with zinc-nickel alloy, followed by nickel and chromium by the method of the present invention, several test pieces are prepared.

Test pieces 223, 225, 357, 358, 360 and 361 are plated according to usual commercial practice using the duplex nickel process as follows.

The semi-bright nickel plate is deposited from a 6 liter "Permalume G" bath (Hanson-Van Winkle-Mun-
ning Co., Matawan, New Jersey). This proprietary semi-bright nickel plating bath contains NiSO_4 , NiCl_2 ,



H_3BO_3 and utilizes proprietary addition agents. The temperature of the bath is maintained at 50° C. and the cathode current density at 50 a.s.f. The semi-bright nickel plate is deposited to a thickness of 1.0 mil at a pH of 3.5.

The overlying bright nickel plate is deposited to a thickness of 0.2 mil in the case of samples 223 and 225, and to a thickness of 0.1 mil in the case of samples 357, 358, 360 and 361, using a commercial 15 liter "Electro-Brite" bright nickel bath (Electrochemicals Inc., Cleveland, Ohio), operated at a cathode current density of 50 a.s.f. This bath uses proprietary addition agents to obtain good bright deposits.

The final chromium plate is deposited, using conforming lead anodes and a standard mixed-catalyst chromium bath such as the following:

Component:	Concentration, g./l.
CrO_3 -----	160
H_2SO_4 -----	.60
H_2SiF_6 -----	5.0

The temperature of the plating bath is maintained at 50° C. and the cathode current density at 180 a.s.f. A bright, micro-cracked plate having a thickness of .03 mil is deposited on samples 223 and 225, whereas a plate of only .01 mil is deposited on samples 358 and 360.

Samples 205, 208, 241, 269, 309, 313 and 314 comprise low-carbon steel as the basis metal on which is deposited successive layers of a bright zinc-nickel alloy, a bright nickel plate and a bright chromium plate according to the method of the present invention. In each instance, the alloy plate is deposited to a thickness of 1.0 mil, using the preferred bath previously given for the alloy plate and in the apparatus previously described. The temperature is maintained at about 45° C., the pH at 6.5 and the cathode current density at 17-25 a.s.f.

The percent nickel in the alloy plate, as determined by analysis, ranges from 13 to 16%.

In order to promote good adhesion between the zinc-nickel alloy layer and the bright nickel deposit, the surface of each sample is "activated" by a 1 minute immersion in a solution containing approximately 0.3 gram of ammonium bifluoride per liter of 2.0% H_2SO_4 by weight. Immersion in the activating solution darkens the surface of the zinc-nickel deposit but has no deleterious effect.

After this activation step the samples are rinsed with water, and then receive a 0.1 bright nickel plate in the apparatus previously described. This plate, which overlies the zinc-nickel alloy plate, is deposited in each instance from the "Electro-Brite" bright nickel electroplating bath previously defined.

These seven samples are now given a water rinse before receiving a bright micro-cracked chromium electroplate. In the case of samples 309, 205, 208 and 313, the plate is deposited to a thickness of 0.01 mil, whereas samples 241, 269, and 314 receive a 0.03 mil micro-cracked chromium plate.

Corrodokote tests are carried out on all the above samples according to the ASTM standard method B380-65. Briefly, this test as applied comprises the procedure of applying a corrosive slurry to the test pieces, permitting the slurry to dry, and exposing the coated pieces to high relative humidity (90-100%) at a temperature of 100° F. for a single 20 hour cycle. After washing and cleaning the test samples, they are developed by exposure

to 90-100% relative humidity for 4 hours. They are then examined to determine the extent of the corrosion.

The samples are rated using the "Ford" rating system which consists of assigning a numerical value for the degree of corrosion sustained by the basis metal, and its appearance. The overall rating is called the "appearance number" and ranges from 0 to 10. A rating of 10 is a perfect score. For further details on the "Ford" method of rating, refer to J. Nasea, Jr., et al., Plating 49, 989 (1962).

PERFORMANCE OF ALLOY-NICKEL CHROMIUM PLATE AND DUPLEX NICKEL-CHROMIUM PLATE IN CORROD-KOTE TESTS

[Deposit thickness, mils]

Sample Number:	Alloy	Bright nickel	Semi-bright nickel	Chromium	Appearance
205-----	1.0	0.1	-----	0.1	9.5
208-----	1.0	0.1	-----	.01	9.4
223-----	-----	0.2	1.0	.03	9.2
225-----	-----	0.2	1.0	.03	9.2
241-----	1.0	0.1	-----	.03	9.0
269-----	1.0	0.1	-----	.03	9.0

The appearance number of 9.2 for duplex nickel-chromium plate (223 and 225), is typical of the rating for that system. The alloy nickel-chromium composite appears to provide the same corrosion protection for steel as the duplex nickel-chromium system. The alloy deposits contain 13-16% nickel.

The Cass test is carried out according to ASTM standard method B368-65. Briefly, it comprises a method primarily applicable to the rapid testing of decorative copper-nickel-chromium or nickel-chromium coatings on steel and zinc base die castings designed for relatively severe service. The cleaned specimens are exposed in a copper-accelerated acetic acid-salt spray fog chamber at 120° F. for 16 hours. The salt solution which is injected into the chamber with compressed air as an atomized spray, is comprised of 5% sodium chloride, acidified with acetic acid to a pH of 3.1-3.3, to which is added 1 gram of cupric chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) per gallon of acid salt solution. The pH is finally readjusted to 3.1-3.3 with acetic acid following the addition of the cupric chloride. After washing and drying the test samples are examined to determine the extent of corrosion. The same "Ford" rating method is used to evaluate the results as used in the Corrodokote tests.

PERFORMANCE OF ALLOY-NICKEL-CHROMIUM AND DUPLEX NICKEL-CHROMIUM IN CASS TESTS

[Deposit thickness, mils]

Sample Number:	Alloy	Bright nickel	Semi-bright nickel	Chromium	Appearance
309-----	1.0	0.1	-----	.01	9.2
313-----	1.0	0.1	-----	.01	9.2
314-----	1.0	0.1	-----	.03	9.3
357-----	-----	0.1	1.0	.03	9.4
358-----	-----	0.1	1.0	.01	9.7
360-----	-----	0.1	1.0	.01	9.8
361-----	-----	0.1	1.0	.03	9.6

The alloy tested was deposited at 17-25 a.s.f. The alloy-nickel-chromium composite and the duplex nickel/chromium systems are essentially equivalent in providing corrosion protection for steel, as scores in excess of 9.0 are generally considered satisfactory and essentially equivalent.

We claim:

1. A method of electroplating a corrodable basis metal which comprises plating said metal with successive deposits of a zinc-nickel alloy, nickel and chromium by the steps of:

(a) directly contacting said metal with an aqueous zinc-nickel electroplating bath maintained at a pH of 4 to 6.8, a temperature of 35° to 60° C. and a cathode current density of 10 to 50 amperes per

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square foot (a.s.f.), said bath containing 1 to 40 grams/liter of nickel ions and 5 to 75 grams/liter of zinc ions for a time sufficient to deposit a zinc-nickel alloy plate containing 10-25% nickel to a thickness of from 0.6 to 1.2 mils;

(b) treating said zinc-nickel alloy plate with an activating bath comprising ammonium bifluoride and sulfuric acid

(c) depositing directly on said zinc-nickel alloy plate, a nickel deposit from an aqueous nickel plating bath maintained at a pH of 1.5 to 5.8, a temperature of 45 to 60° C., and a cathode current density of 18-94 a.s.f., said bath containing 47-107 g./l. of nickel ions, for a time sufficient to deposit said nickel plate to a thickness of from .05 to 0.25 mil;

(d) depositing on said nickel plate a chromium deposit from an aqueous chromium plating bath maintained at a temperature of 30 to 100° C., and a cathode current density from 70 to 1200 a.s.f., said bath containing 57 to 583 g./l. of chromic acid, and a suitable amount of catalyst ions for a time sufficient to deposit said chromium plate to a thickness of from 0.005 to 0.05 mil.

2. The method of claim 1, wherein the zinc-nickel bath composition comprises the following:

	G./l.
Ammonium chloride	200-275
Zinc oxide	10-23
Nickel chloride (NiCl ₂ ·6H ₂ O)	22-50
Boric acid	15-25

3. The method of claim 2, wherein the zinc-nickel bath additionally contains a brightener.

4. The method of claim 3, wherein the brightener is selected from the group consisting of dextrine, thiourea, peptone, gelatin, naphthol disulfonic acid, coumarin and saccharin.

5. The method of claim 2, wherein the bath contains a wetting agent.

6. The method of claim 5 wherein said wetting agent is selected from the group consisting of sodium lauryl sulfate, alkyl substituted benzene sulfonates, sodium lauryl sulfoacetate, sodium monolaurin monosulfate, the sodium salt of lauric acid monoester of diethylene glycol and dodecyloxymethane sulfonate.

7. The method of claim 2 wherein the operating conditions for the zinc-nickel plating bath lie within the following limits:

pH: 5.8-6.8
Temperature: 40°-55° C.
Cathode current density: 10-40 a.s.f.
Zinc ions: 8-18.5 g./l. and
Nickel ions: 5.4-12.3 g./l.

8. The method of claim 1 wherein the electrolytic bath is agitated and continuously filtered.

9. The method of claim 1 wherein the plating current used in plating the zinc-nickel alloy is proportioned be-

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tween the zinc and nickel anodes so as to maintain a constant zinc-nickel ratio in the bath, this ratio being maintained between 0.5 and 1.5.

10. A method of electroplating a corrodable basis metal which comprises plating said metal with successive deposits of a zinc-nickel alloy, nickel and chromium by the steps of:

(a) contacting said metal with an aqueous zinc-nickel electroplating bath maintained at pH of 4 to 6.8, a temperature of 35° to 60° C. and a cathode current density of 10 to 50 amperes per square foot (a.s.f.), said bath containing 1 to 40 grams/liter of nickel ions and 5 to 75 grams/liter of zinc ions, for a time sufficient to deposit said zinc-nickel alloy to a thickness of from 0.6 to 1.2 mils, said bath comprising the following composition:

	G./l.
Ammonium chloride	200-275
Zinc oxide	10-23
Nickel chloride (NiCl ₂ ·6H ₂ O)	22-50
Boric acid	15-25

(b) treating said zinc-nickel alloy plate with an activating bath comprising 0.2 to 0.4 gram of ammonium bifluoride per liter of 1.4 to 2.2% sulfuric acid;

(c) depositing on said activated zinc-nickel alloy plate, a nickel deposit from an aqueous nickel plating bath maintained at a pH of 1.5 to 5.8, a temperature of 45° to 60° C., and a cathode current density of 18-94 a.s.f., said bath containing 47-107 g./l. of nickel ions, for a time sufficient to deposit said nickel plate to a thickness of from 0.05 to 0.25 mil;

(d) depositing on said nickel plate a chromium deposit from an aqueous chromium plating bath maintained at a temperature of 30° to 100° C., and a cathode current density from 70 to 1200 a.s.f., said bath containing 57 to 583 g./l. of chromic acid and a suitable amount of catalyst ions, for a time sufficient to deposit said chromium plate to a thickness of from 0.005 to 0.05 mil.

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